

AD-A155 561 MULTIPHOTON PRODUCTION AND DETECTION OF ATOMS(U) OREGON 1/1
UNIV EUGENE P C ENGELKING 01 APR 85 ARO-18047. 1-CH
DAAG29-81-K-0154

UNCLASSIFIED

F/G 7/5

NL

END

FORMED

END



4

2

MULTIPHOTON PRODUCTION AND DETECTION OF ATOMS

AD-A155 561

FINAL REPORT

PAUL C. ENGELKING

1 APRIL 1985

U.S. ARMY RESEARCH OFFICE

DAAG29.81-K-0154 P-18047-CH

UNIVERSITY OF OREGON

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

THE VIEW, OPINIONS, AND/OR FINDINGS CONTAINED IN THIS REPORT ARE THOSE OF THE AUTHOR AND SHOULD NOT BE CONSIDERED AS AN OFFICIAL DEPARTMENT OF THE ARMY POSITION, POLICY, OR DECISION, UNLESS SO DESIGNATED BY OTHER DOCUMENTATION.

DTIC FILE COPY

6 6 0 7 6

RECEIVED
JUN 25 1985

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ARO 18047.1-CH	2. GOVT ACCESSION NO. AD-A155361	3. RECIPIENT'S CATALOG NUMBER N/A
4. TITLE (and Subtitle) Multiphoton Production and Detection of Atoms		5. TYPE OF REPORT & PERIOD COVERED Final 1 Aug 81 - 31 Jan 85
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Paul C. Engelking		8. CONTRACT OR GRANT NUMBER(s) DAAG29-81-K-C154
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Oregon Eugene OR 97403		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		12. REPORT DATE 1 April 1985
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) NA		
18. SUPPLEMENTARY NOTES The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Multiphoton dissociation phosphorous ionization sulfur, detection iron atoms LA		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The production of atomic fragments from a compound using multiphoton dissociation was investigated for metal centered and hetero atom centered compounds. The atoms were detected by multiphoton ionization. Metal centered systems generated large amounts of the characteristic metal atoms, with a large kinetic energy release, indicating a direct dissociation Mechanism. P and S centered systems gave mainly diatomic fragments.		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)



FINAL REPORT
Multiphoton Production and Detection of Atoms

ARO proposal number: P-18047-CH
Period: 1 Aug 81 -- 31 Jan 85
Title: Multiphoton Production and Detection of Atoms
Contract: DAAG29.81-R-0154
Institution: University of Oregon
Author: Paul C. Engelking

Accession For	
NTIS Grant	
D. J. T. B.	
Unan. 100000	
Justified	
By	
Distribution	
Availability	
Avail. and	
Dist	Special
A-1	

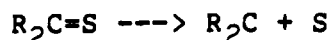
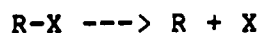
1.0 Research Problem:

When a compound is probed by a high intensity laser field, it may multiphoton dissociate (MPD), giving atomic or radical fragments. Atoms may be detected by subsequent multiphoton ionization (MPI) with very high sensitivity. Thus MPD/MPI is potentially a very sensitive detection technique for classes of compounds containing specific elements. There are two questions addressed by this research. First, what is the mechanism by which a central atom may shake off its surrounding chemical groups, becoming a naked atom? Second, which classes of compounds will give bare atoms in a multiphoton dissociation event?

2.0 Major Results:

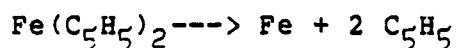
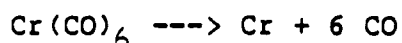
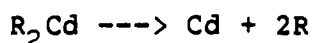
2.1 Types of atoms generated.

Others have shown that atoms may be generated by MPD if they are in terminal positions in a molecule. For example,



readily occur in multiphoton dissociation.

It is more of a question whether a central atom can shake off its surrounding atoms or groups. Surprisingly, many atoms can, when bound in a central position in a molecule. For example,



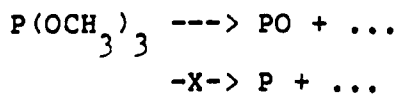
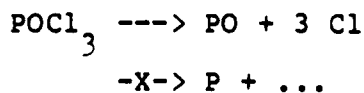
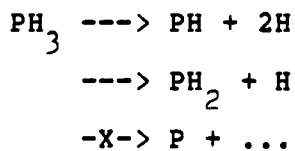
So far most examples of this behavior have been of metal atoms surrounded by ligands. Both covalent and ionic bonding can be broken, as can both covalent sigma and pi type bonds. The bonds may be cleaved either separating the electrons, or leaving them paired on one fragment. Early in this research we demonstrated that photodissociation of metal ligand analogues of ferrocene would cleanly photodissociate to give metal atoms, producing atomic cobalt, ruthenium, nickel, etc. This behavior seems to be general for the transition elements, all of which are metals.

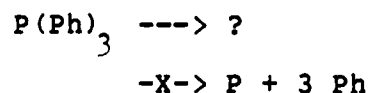
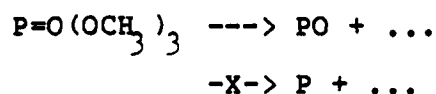
This general behavior might be explained by the large d-ligand electron transfer cross sections for photabsorption, promoting an electron from a metal non-bonding orbital into a ligand-metal antibonding orbital. This leads to rapid

dissociation of the metal ligand bond. Since almost all organometallic compounds have this type of bonding, we now expect this dissociation to be general for this whole class.

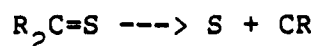
In contrast to metal centered compounds, compounds having main group heteroatoms at their centers do not appear to readily produce the bare hetero atom in MPD. The electronic transitions in these compounds do not prepare dissociative states in all cases. While one or more atoms or groups may be shaken off by a central phosphorous or sulfur, removal of at least one subsequent group usually becomes difficult. Thus, diatomic fragments are often the smallest fragments of MPD in this class of compounds.

We have examined quite a few cases of this, and feel confident in the generality of the principle. For example, we have determined the following:

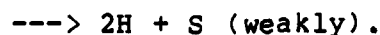
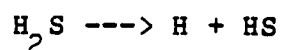
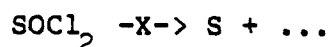
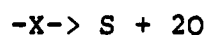
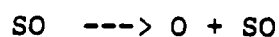




This is also true of sulfur compounds. While terminal sulfur is easily ejected



central sulfur is difficult to produce:



These measurements were made under conditions of high excimer laser fluxes near 248 and 352 nm, in addition to the wavelengths of probing dyelaser wavelengths between 500 and 3500 nm. Phosphorous atoms were detected only in the experiments with triphenyl phosphine and phosphine, only at high pressures, with a long-pulse (1 microsecond) laser. Sulphur atoms were weakly detected in the same region as the SO D-X bands in the near UV, but the atomic three-photon Rydberg transitions were orders of magnitude weaker than the signals

resulting from SO MPI.

We attribute P atom production to result from a collision process in the gas at about one torr pressure. It may be possible to produce atoms by collisional assisted chemistry in a MPD process, but we did not further explore this.

The striking result of this work was the prevalence of both PO and SO from a wide variety of precursors. These diatomic fragments serve as characteristic markers for the atoms P and S in oxygen containing compounds. This should not be too surprising, since two "atomic emission" bands characteristic of phosphorous are really the gamma and beta bands of PO.

2.2 Diatomic fragments.

The non-metal-centered compounds usually resulted in the central atom bound in a diatomic instead of a naked atom. These diatomics were identifiable by their own characteristic MPI spectra. Several interesting effects were observed in a MPI spectrum of the diatomics that are not observed in straight absorption spectra.

The first PO MPI spectra were observed by Smyth and Mallard [JCP 77, 1779 (1982)] in flames. They report that

"the intensities of the observed signals vary in an unexpected fashion for transitions which reach the same vibrational level of the resonant intermediate state". They speculated that the ionization step was highly structured, due to a second intermediate state used in a resonant ionization process by the second photon. We have observed this effect in three cases: PO, SO, and NO. At high resolution the effect is very striking, giving "atomic like" intense resonance peaks within a molecular rotational band.

Our analysis of NO established the nature of the effect. The first resonant step activates the molecule in a particular vibrational and rotational level of an excited electronic state. If another state above this has a rotational level within the laser bandwidth, the molecule can make another resonant transition to that higher state, and then subsequently ionize. In NO this second resonant state is a previously uncharacterized Rydberg state, which we subsequently characterized.

The MPI spectra of not only NO, but SO and PO are dominated by uncharacterized states. The molecules may be prepared by MPD in excited states, from which transitions are poorly understood, or the transitions from the lowest states are strongly influenced by poorly characterized states. In SO, the D state is a strong feature in the near

UV. This state is dissociative, but appears quite structured in our experiments, primarily because the MPI probes the molecule before it dissociates.

Several transitions in SO are presently unassigned in our experiments. These probably originate in the poorly understood metastable SO state. Ashfold et.al., in their work on MPD/MPI on phosphine [Chem. Phys. Lett. 111, 226 (1984)] report that the dominant transition observed in the near UV could not be understood until publication of our work on PH [JCP 80, 5926 (1984)]. We concur with their assessment that "the observation of weak inter-combination bands such as the b-X systems of NH and PH is vital..."

The original aim of detecting heteroatom compounds by MPI/MPD could be modified away from atomic MPI detection to the MPI detection of diatomic fragments instead. Thus, MPD/MPI would be moving in the direction of MPIFF [D.S. Frankel, ACS presentation, Hawaii, 1984]. However, more spectroscopy would have to be done on the diatomics in order to place this procedure on a firm scientific footing.

C. Mechanism of metal centered MPD

Metal centered compounds such as ferrocene can eject their ligands in a MPD process to leave a clean metal atom. We have speculated that this process is driven by direct

dissociation of repulsive electronic states. If this is so, significant amounts of translational energy should appear in the fragments as they bobsled down the potential slope that serves to separate the fragments.

Ferrocene is especially interesting, because of its high symmetry. The iron, located in the center of the molecule, will not receive any net momentum if the dissociation is fast and symmetrical. Only if the molecule's MPD process breaks the symmetry will the iron receive recoil momentum. Thus, monitoring the Fe velocity in a MPD experiment on ferrocene will show a significant amount of recoil energy given to the iron only if the process is directly dissociative and breaks the symmetry during the dissociation.

We set out to test this by monitoring the Fe recoil by doppler MPI. The amount of recoil surprized us. We were looking for a small effect, and the results we finally obtained showed the iron with an amount of energy consistent with a statistical distribution of energy in all three translational motions of the fragments. Hardly any energy is used for excitation of rotation or vibration of the cyclopentadienyl rings. Thus, the dissociation is direct, and not a slow, "unimolecular decay" of a hot ferrocene shaking off its ligands. There does not appear to be enough

time for the energy to degrade into vibrational motion of the radical. The dissociation is also highly "non-concerted", since the molecular central symmetry is strongly broken.

This recoil of the iron atom has a significance for detection by MPI. The linewidths are set by two effects: (1) lifetime broadening of the resonance, and (2) doppler broadening of the recoiling atom. We have found that the doppler width is intrinsically large, on the order of 0.2 cm⁻¹ in our particular case.

If MPI is to be made quantitative, the linewidth effects will have to be understood. We have made progress to understanding these effects in this model system.

2.3 Multicolor MPD/MPI

We have also extensively investigated the use of two laser wavelengths simultaneously in one experiment. We have probed ferrocene MPD by mixing an excimer laser beam with a beam from a dye laser. We have found that strong enhancement of several MPI features resulted. At 248nm, the iron atoms are resonantly enhanced for an ionization without the dye laser, and a one-laser detection scheme is possible, even without a dye laser. At 352nm, the addition of the excimer laser pulse enhances the dissociation of the ferro-

cene, and by making other transitions resonant, brings new features to the the spectrum.

In addition to the gas cell experiments, several MPI experiments were performed on ferrocene in a pulsed nozzle, mass-spectrometer apparatus. The ions observed were predominantly Fe^+ , with some Cp^+ and mixed clusters of Iron and Cp ligands. Negative ions were also observed, with the major species being Cp^- . This appears not to be the result of a direct heterolytic dissociation, but rather results from e^- attachment to FeCp . Very large cross sections have been observed for dissociative attachment to metallocenes [J. Moore, private communication].

2.4 Conclusions

Multiphoton dissociation of metal centered systems produces metal atoms.

Dissociation is probably direct, via repulsive surfaces in the upper electronic states.

In at least one case, ferrocene, the dissociation surface is quite complex, since the dissociation breaks the symmetry. Energy is imparted to the iron.

The iron energy is consistent with energy partitioning

only into translations in the metallocene decomposition.

In contrast to the metal centered systems, heteroatom centered systems appear to resist dissociation to the bare central atom.

The usual terminal fragments observed in hetero atom compounds are diatomics; e.g. PO, PH, SO, NO, ...

The diatomic molecular fragmnets are prepared by dissociation, often in spectroscopically uncharacterized states.

The diatomic MPI transitions that are observed are often spectroscopically uncharacterized as of the present.

3.0 Publications

"Two color multiphoton dissociation and ionization of ferrocene," H. T. Liou, Y. Ono, P.C. Engelking, and J. T. Moseley (in prep).

"MPD/MPI of ferrocene: Atomic iron recoil," H.T. Liou, Y. Ono, P. C. Engelking and J.T. Moseley (in prep).

"Double enhancement in the MPI of NO," T.C. Steimle and H.T. Liou, Chem Phys. Lett. 100, 300 (1983).

"The emission spectrum of BrCN+," P.G. Carrick, S. Brossard, and P.C. Engelking, (in prep).

"Atomic sulfur in the MPD/MPI of SO₂," H.T. Liou, Y. Ono, P.C. Engelking and J.T. Moseley, (in prep).

Copies will be supplied as available.

4.0 Personnel Supported

Dr. Patrick Carrick

Dr. Yoshi Ono

Dr. Fred Grieman

Hui-Tarng Liou

Stan Brossard

Barbara Eisenberg

Michelle Siggel

Mr. Liou expects to receive a Ph.D. in physics in 1985:
an abstract for his thesis has been submitted to the graduate school.

END

FILMED

7-85

DTIC